Synthesis and structure of a stuffed derivative of α-quartz, Mg0.5AlSiO4

HONGWU XU,1,* PETER J. HEANEY,2 PING YU3 AND HUIFANG XU4

1Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.
2Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.
3Nuclear Magnetic Resonance Facility, University of California at Davis, Davis, California 95616, U.S.A.
4Department of Geoscience, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

ABSTRACT

A structural derivative of quartz with the composition Mg0.5AlSiO4 has been grown from glass and characterized using synchrotron X-ray diffraction (XRD), transmission electron microscopy (TEM), and 29Si nuclear magnetic resonance (NMR) spectroscopy. Rietveld analysis of the XRD data indicates that the framework of Mg0.5AlSiO4 is isostructural with α-quartz, rather than β-quartz, as is consistent with previous theoretical modeling (Sternitzke and Müller 1991). Al and Si exhibit long-range disorder over the framework tetrahedral sites, indicated by the absence of the superlattice reflections corresponding to the doubling of c relative to that of quartz. Nevertheless, 29Si NMR measurements show that Al and Si exhibit partial short-range order with an ordering degree of 56%. Electron diffraction reveals superlattice reflections indicative of doubled periodicities along the a-axes. Fourier electron density maps show that Mg occupies channel sites that each are bonded to six O atoms, in contrast to the tetrahedral coordination of Li in the β-quartz-type framework for β-eucryptite, LiAlSiO4. Furthermore, the concentrations of Mg in adjacent channels are different, resulting in framework distortions that generate the superstructures along a.

Keywords: Quartz, eucryptite, stuffed derivative, synthesis, crystal structure, synchrotron X-ray diffraction, transmission electron microscopy, nuclear magnetic resonance spectroscopy

INTRODUCTION

As one of the densest framework minerals, quartz has a low tolerance for the incorporation of alien cations into its structure. In natural quartz, there exist only trace amounts (mostly at the levels of hundreds of parts per million) of extraneous ions such as Al3+, Fe3+, and Na+ (Keith and Tuttle 1952; Ghiorso et al. 1971). In particular, lithium is considered the most common extraneous cation amongst the above, which has been used to partially replace Li+ (Petzoldt 1967; Beall 1994). Moreover, other small cations, mainly Mg2+ and Zn2+, have been used to partially replace Li+ (Petzoldt 1967; Beall 1994). Nevertheless, 29Si NMR measurements show that Al and Si exhibit partial short-range order with an ordering degree of 56%. Electron diffraction reveals superlattice reflections indicative of doubled periodicities along the a-axes. Fourier electron density maps show that Mg occupies channel sites that each are bonded to six O atoms, in contrast to the tetrahedral coordination of Li in the β-quartz-type framework for β-eucryptite, LiAlSiO4. Furthermore, the concentrations of Mg in adjacent channels are different, resulting in framework distortions that generate the superstructures along a.

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* E-mail: hxu@lanl.gov